Molecular Variables in the Self-Assembly of Supramolecular Nanostructures

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ABSTRACT: Supramolecular structures have the potential to provide macromolecular behavior using relatively low molar mass building blocks. We present here data on the self-assembly of triblock rodcoil molecules which contain a rigid biphenyl ester segment covalently linked to structurally diverse oligomeric segments. These molecules form supramolecular aggregates with molar masses in the range $10^5$–$10^6$ Da, and our experiments probe how supramolecular structure can be manipulated by varying the volume fraction of the coillike flexible segments with respect to that of rod segments. The oligostyrene–oligoisoprene diblock coils were synthesized via anionic polymerization and varied in average length from $(6_{sty},6_{iso})$ to $(30_{sty},30_{iso})$. Small-angle X-ray scattering scans revealed layer spacings corresponding to monolayers that increase in size as the coil’s molar mass increases. We observed that an increase in coil volume fraction reduces the thermal stability of the supramolecular structure, but a corresponding increase in rod segment length can counteract this effect. Finally the self-organized nanostructures seem to pack into a superlattice based on evidence obtained by X-ray scattering and transmission electron microscopy.

Introduction

We believe supramolecular assemblies of nanoscale dimension and molar mass in the range $10^5$–$10^6$ Da could be useful in the design of novel functional materials. The challenge is to learn how to control the spontaneous formation of such large aggregates by encoding the size and shape information in precursor molecules. Our grasp of some of the variables that control nanostructure formation is essential to design libraries of functional materials. Since materials generally express their functionality in macroscopic forms, this vision requires also an understanding of the packing and networking of such nanostructures in three dimensions.

Supramolecular chemistry seeks to control the formation of intermolecular bonds and we are only beginning to discover the design rules behind noncovalent assembly. The formation of small aggregates of molecules was investigated by Whitesides and co-workers.1–3 Also, Lehn4 and Meijer5 demonstrated the formation of 1D mushroom shaped nanoaggregates in our laboratory8 as well as other work including self-assembled blends,9 dendritic polymers synthesized via self-assembly,10,12 and finally polymerized self-organized vesicles.13 These examples of nonlinear architectures are only a small fraction of the possibilities that supramolecular chemistry might offer in creating molecular object polymers. The ultimate goal herein should be to mimic the great functionality behind shape persistence in proteins.

Our laboratory has studied a variety of building blocks for materials in order to understand some of the central issues in the creation of supramolecular materials. We first reported on the combined use of self-organization and chemical reaction in chiral monomers to generate two-dimensional polymers.6,7 We have also investigated the formation of nanostructures by self-assembly using rodcoil polymers,14–16 so named because they have a rigid molecular segment covalently attached to a very flexible segment. Other work in the literature has focused on phase separation in high molecular weight rodcoil block copolymers.17–19 Our work has targeted small molecules with rodcoil architecture as an approach to create nanoobjects with defined shapes. Furthermore, in contrast to conventional rodcoil polymers our rodcoil toolbox consists of molecules in which the rod segments have the molecular precision of organic compounds. Our recent report on these systems demonstrates they can form supramolecular materials with novel properties.

Crystallization and steric in systems with rodcoil architecture are key factors in the formation of controlled supramolecular objects. We currently believe the energetic interplay between crystallization, coil entropy, and the repulsive energies associated with steric elements can lead to finite supramolecular objects with fairly defined size and shape. Biphenyl ester segments are the principal building blocks for the rigid rod segment, and these have a strong propensity to crystallize with $\pi-\pi$ stacked arrangements. In contrast, the oligostyrene and oligoisoprene coil segments are structurally diverse and hence unable to crystallize.9 Finally the cross sectional area of the polystyrene chain is significantly larger than that of the biphenyl rod resulting in steric interactions. As these energetic terms balance, the size and shape of the supramolecular structure is defined. In this investigation, we have concentrated on the fundamental theme of understanding this energetic interplay. This was accomplished by varying the coil length and size as well as rod length and observing how such changes affect ordering behavior and structure.
Results and Discussion

Rodcoils 1a–1f were synthesized as described in the experimental procedure and then analyzed with polarized light microscopy, SAXS, and TEM to investigate their solid state structure. These materials are birefringent solids under cross polarizers in the optical microscope. Upon heating, they undergo a transition to a liquid crystalline state followed by isotropization. In the liquid crystalline state, these materials are highly viscous suggesting a smectic phase, and this is also supported by their optical texture and small-angle X-ray diffraction. Interestingly, related work in our laboratory found evidence for the presence of aggregates in the liquid crystalline state.20,21 As indicated in Table 1 the isotropization temperature of 1a is 251 °C, similar to 1b,8 as measured by differential scanning calorimetry (DSC), a temperature that agrees with observations by optical microscopy. Interestingly, related work in our laboratory found evidence for the presence of aggregates in the liquid crystalline state.20,21 As indicated in Table 1 the isotropization temperature of 1a is 251 °C, similar to 1b,8 as measured by differential scanning calorimetry (DSC), a temperature that agrees with observations by optical microscopy. Interestingly, related work in our laboratory found evidence for the presence of aggregates in the liquid crystalline state.20,21 As indicated in Table 1 the isotropization temperature of 1a is 251 °C, similar to 1b,8 as measured by differential scanning calorimetry (DSC), a temperature that agrees with observations by optical microscopy. Interestingly, related work in our laboratory found evidence for the presence of aggregates in the liquid crystalline state.20,21

Table 1. Characterization of Rodcoil Materials

<table>
<thead>
<tr>
<th>molecules</th>
<th>extended length (nm)</th>
<th>isotropization temp (°C)</th>
<th>SAXS d spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a (6sty, 6iso)</td>
<td>7.7</td>
<td>251</td>
<td>7.3</td>
</tr>
<tr>
<td>1b (9stry, 9iso)</td>
<td>9.6</td>
<td>250</td>
<td>7.4</td>
</tr>
<tr>
<td>1c (13stry, 14iso)</td>
<td>12.6</td>
<td>185</td>
<td>8.4</td>
</tr>
<tr>
<td>1d (12stry, 20iso)</td>
<td>14.7</td>
<td>185</td>
<td>8.9</td>
</tr>
<tr>
<td>1e (20stry, 12iso)</td>
<td>13.6</td>
<td>160</td>
<td>8.4</td>
</tr>
<tr>
<td>1f (30stry, 30iso)</td>
<td>23.2</td>
<td>none</td>
<td>none</td>
</tr>
</tbody>
</table>

X-ray studies of these materials were carried out in order to determine how the solid-state structure varied with the relative dimensions of the two blocks of the coil segment. SAXS scans of rodcoil films cast on glass from a 1 mg/mL chloroform solution and then annealed at 125 °C for 2 h showed interesting results. The (6stry, 6iso) derivative 1a had a sharp SAXS peak at 73 Å, a similar periodicity to that of 1b which revealed a (001) d spacing of 74 Å. The observation that increasing the coil length from (6stry, 6iso) to (9stry, 9iso) does not change the system’s periodicity suggests that significant splaying of coils occurs over the rod clusters. It is important to note that from tilt angle calculations based on second harmonic generation experiments molecules 1b are standing perpendicular to the layer.22 The fact that layer periodicity does not drastically change from (9stry, 9iso) to (6stry, 6iso) coils also suggests that a certain extent of molecular stretching is forced on the system by rod crystallization. If the (6stry, 6iso) and (9stry, 9iso) systems have a similar volume of constrained segments, then the longer coils simply fold closer to the bottom of the nanostructures and do not change their height.

Characterization of rodcoil 1a with TEM revealed the presence of nanocrystals (Figure 1). The samples were prepared without any special stains and therefore the contrast observed is due to diffraction and phase contrast in the samples themselves. Dark regions represent the crystallized rod clusters while the light regions surrounding each nanocrystal are regions containing the amorphous coil segments excluded from nanocrystals. Within some areas of the image the amorphous domains are too large to contain only a coil segment, and it is believed that these areas are comprised of rodcoils in a liquid crystalline glassy state.

Figure 1. Transmission electron micrograph of rodcoil 1a with an average of 6 units of isoprene and 6 units of styrene in the coil (a) and of 1b with an average of 9 units of isoprene and 9 units of styrene (b). The shorter coil leads to more polydisperse and disordered nanostructures.
can be indexed as two peaks corresponding to the parameters of 6.6 nm by 7.0 nm and an angle $\beta = 110^\circ$. Therefore, the broad scattering intensity centered at 6.4 nm can be indexed as two peaks corresponding to the (100) and (010) reflections with close agreement to the calculated values of 6.2 and 6.5 nm, respectively. The peak broadening could be due to a small coherence length as well as a lack of 3D ordering. As previously mentioned, there is limited correlation of the nanostructures in three dimensions as is evident by the drastic loss of contrast in TEM images of multilayer samples. We can therefore assume that nanostructures form 2D lattices layered on top of one another with no interlayer correlation. This structure would be very similar to those observed for DNA–lipid bilayer assemblies in which DNA chains form a 2D smectic phase but lack 3D correlation.23–25 Reflections associated with the DNA smectic layers were observed experimentally23,24 and predicted theoretically25 to be broader and weaker in intensity due to the lack of correlation along the $z$ direction. This behavior will manifest itself in our system by the broadening of both the (100) and the (010) reflections. Therefore, it is reasonable to suggest that the angular resolution of these reflections is lost and the peaks merge into one centered at 1.4 deg in $2\theta$.

To investigate the thermodynamic stability of the layered structures formed by the triblock self-assembling molecules of interest here, a variable temperature experiment was carried out. By rapid precipitation of 1b out of chloroform solution through the addition of methanol, an amorphous glassy solid forms. Interestingly, however, upon annealing the system rapidly self-organizes into a layered structure. This is clearly revealed by the variable temperature SAXS scans shown in Figure 4. Note the lack of order at 23 and 75 °C and the subsequent appearance of a peak corresponding to a $d$ spacing of 74 Å at higher temperatures. This peak continues to rise in intensity as the temperature is increased, and at 250 °C it disappears, in agreement with observations by optical microscopy which indicate that isotropization occurs between 225 and 250 °C. Most importantly, if the sample is slowly cooled from 200 °C the order remains, implying that the stable organization at room temperature is layered and not glassy. Furthermore, molecule-solvent interactions should play an important role in the kinetics of self-assembly in these systems.

SAXS of 1c reveals a sharp peak at 84 Å as well as a broad and very weak peak corresponding to a $d$ spacing of 50 Å. The broad peak at 50 Å is possibly associated with the distance between nanoggregates within the plane of the film. The (001) $d$ spacing increases as the
A coil structure is changed from (9 sty, 9 iso) to (13 sty, 14 iso) in 1b and 1c respectively, an expected result considering the increase in molecular length. A further increase in coil length in 1d and 1e results in greater layer periodicities. Figure 5 shows a plot of the layer periodicity in 1a-1f, which reflects the height of nanostructures, as a function of the extended length of the corresponding average-sized molecules. The first important feature of the plot in Figure 5 is the fact that d spacings are always significantly smaller than extended molecular lengths. This observation offers partial evidence for the mushroom-like nature of the nanostructures lacking $D_{\infty h}$ symmetry. In other words, the plot would not support the formation of dumbbell-like symmetric nanostructures formed either through interdigitation of the rod segments or through strong stem-to-stem interactions between two mushroom-like nanostructures. Such packing arrangements would generate larger d spacings in SAXS scans. Also, these packing arrangements do not successfully fill free volume as was discussed elsewhere. Second, the deviation from a slope of 1 suggests that partial folding of coils occurs over the rod clusters thus defining the mushroom architecture. Therefore, infinite layers of nearly extended molecules, as commonly occurs in smectic phases, do not seem to form here. The implication is that finite supramolecular clusters are the basic constituents of these solids. Interestingly, the linearity of the data strongly suggests non-Gaussian behavior within the coils providing insight into the constrained environment these chains experience, for example, stretching of flexible units attached to rod segments.

We investigated the self-assembling behavior of a rodcoil system containing a shorter rod segment than all other materials studied here. The first rodcoil synthesized was the (9 sty, 9 iso) system with only two biphenyl units in the rod segment (2). SAXS of 2 showed a weak, broad signal at 70 Å but these molecules do not appear to have the same strong ordering ability as the 3 biphenyl unit homologues (1b). Therefore, molecules were synthesized which contained the same number of biphenyl units as 2 and coil lengths of only (5 sty, 5 iso) (3). After annealing, rodcoil 3 showed a sharp SAXS (001) peak at 60 Å and an (002) peak at 30 Å. When the coil length remains the same but only 1-biphenyl unit is attached to the coil (4), the material does not form an ordered solid as revealed by the absence of birefringence when examined under the optical microscope.

Transmission electron microscopy studies of 3 gave interesting results. The micrograph (Figure 6) shows 20–25 nm aggregates dispersed throughout the film. The electron diffraction inset shows that these aggregates are crystalline with a unit cell identical to 1b (orthorhombic with lattice parameters a = 8.2 Å and b = 5.6 Å). The 20–25 nm crystalline aggregates are much larger than those observed in 1b (5 nm aggregates). This suggests that repulsive forces among the short (5 sty, 5 iso) coil segments are dramatically reduced allowing further growth of the crystalline aggregates of rod segments. However, not all of the material forms these crystallites as can be observed in the micrograph (the micrograph was taken at focus with an objective aperture). The objective aperture generates contrast by eliminating diffracted beams while maintaining transmitted beams. In this configuration, any species that strongly diffracts electrons appears dark (the aggregates observed) and the lighter regions that transmit a majority of the electrons are amorphous. This amorphous component is also observable in the electron diffraction pattern where an amorphous halo is clearly visible. The aggregate–aggregate spacing is ~50 nm, a distance far larger than that which can be attributed to the stretching and splaying of the coils. Therefore, there must be noncrystalline material within this region. Perhaps the short segments of the Poisson distribution are aggregat-
The electron diffraction pattern shows Debye rings corresponding to the (110), (200), and the (210) reflections. The 5 unit oligoisoprene coil. The image is unstained, and therefore the contrast is derived from diffraction and phase contrast. The electron diffraction pattern shows Debye rings corresponding to the (110), (200), and the (210) reflections. 

Experimental Section

The \(^1\)H and \(^{13}\)C NMR spectra were obtained using Varian U400 and U500 spectrometers in the indicated solvents; chemical shifts are expressed in parts per million (\(\delta\)) using residual solvent protons as an internal standard. Splitting patterns are designated as follows: s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, m = multiplet, and b = broad. Analytical thin-layer chromatography (TLC) was performed on KIESEL GEL F 254 precoated TLC plates. Silica for column chromatography was Silica Gel 60 (230–400 mesh) from EM Science. Gel permeation chromatography (GPC) analyses were performed in THF using a Waters 600E instrument equipped with UV and refractive index detectors. Differential scanning calorimetry (DSC) was carried out in a TA Instruments model 2920 calorimeter and in all scans heating and cooling rates were 10 °C/min. Polarized optical microscopy utilized a Leitz Laborlux 12POL optical microscope equipped with a Hi-Star area detector and Bruker (Siemens) SAXS software mounted on an M18X-HF22 SRA rotating anode generator. Powder diffraction rings were integrated over 360° to yield the patterns and were calibrated using a silver behenate standard. Transmission electron microscopy (TEM) studies were performed on a Phillips CM 200 TEM operating at 120 kV accelerating voltage using bright field imaging. Samples were prepared by casting from chloroform solution onto a water surface and then transferring the resulting films to copper TEM grids and analyzed without annealing. The samples are beam sensitive, and contrast is lost during longer electron beam exposures.

Unless otherwise noted, all starting materials were obtained from Aldrich and used without further purification. Dry styrene, isoprene, dichloromethane, and N,N-dimethylformamide (DMF) were obtained by vacuum transfer from calcium hydride. Dry tetrahydrofuran (THF) and benzene were obtained by vacuum transfer from sodium and benzophenone. Diisopropylcarbodiimide (DIPC) was distilled before use. 4-(N,N-Dimethylaminopyridinium-4-toluenesulfonic acid (DPTS) was prepared using a published procedure. 

\(4'\)-Hydroxy-4-(dimethylthexyloxyisopropylene) Carboxylate. Morpholine (2.2 mL, 23.0 mmol, \(\delta\) 0.999), \(4'\)-hydroxy-4-biphenyl carboxylic acid (5.0 g, 23.3 mmol), and dimethylformamide (20 mL) were placed in a flask and stirred. (Dimethylthexyloxy)isophorone (4.5 mL, 23.0 mmol, \(\delta\) 0.909) was added and the solution was stirred at room temperature for 30 min. The resulting mixture was diluted with dichloromethane (100 mL), washed with saturated aqueous sodium bicarbonate (200 mL), and water (200 mL), and then dried over MgSO\(_4\). The solvent was removed by rotatory evaporation and the product was purified by column chromatography (CH\(_2\)Cl\(_2\)).
to give a tacky, white solid. Yield: 7.3 g (80%). 1H NMR (CDCl3): δ 8.09 (d, 2H), 7.62 (d, 2H), 7.52 (d, 2H), 7.00 (d, 2H), 6.90 (br, 1H), 1.81 (m, 1H), 0.97 (m, 12H), 0.48 (s, 6H).

(6,6)-Carboxylated Oligo(styrene-b-isoprene). Benzene (50 mL), THF (5 mL), and styrene (5 mL, 43.7 mmol, δ 0.909) were placed in a flask and the solution was degassed by a freeze–pump–thaw cycle using liquid nitrogen. n-BuLi (1.6 M inhexanes, 3.9 mL, 6.2 mmol) was added with rapid stirring.27 Then, stirring deep red color for 5 min, and then the solution was decanted away from the unreacted magnesium turnings. The ether solution was washed with 1 N HCl (200 mL) and water (500 mL) and the addition was complete, the mixture was refluxed for an additional 2 h. The reaction was quenched by bubbling carbon dioxide through the solution for 5 min. Acidic stirring (3.82 mL, 51.2 mmol, ethylthexylsilyloxy)biphenyl (10.0 g, 25.6 mmol), ethyl bromide (1.1 g, 60%). 1H NMR (CDCl3): δ 8.32 (d, 2H), 7.68 (d, 2H), 7.60 (m, 4H), 7.38 (d, 2H), 7.30 (d, 2H), 6.35–7.25 (m, 50 H), 4.41–5.26 (m, 12H), 1.01–2.41 (m, 116H), 0.92 (s, 12H), 0.30 (s, 6H). GPC (THF): PDI 1.07; M, 1920.

4-[4-(4-Hydroxy-4-biphenyl)carboxyloxy]biphenyl Poly(styrene-b-isoprene) 4-Carboxylate (2 and 3). Tetrahydrofuran (20 mL) and 4-[4-(dimethylthexylsiloxy)-4-biphenyl]-carboxyloxy)biphenyl poly(styrene-b-isoprene) 4-carboxylate (1.1 g, 0.5 mmol) were placed in a round-bottom flask and cooled to –78 °C in a dry ice/acetone slush bath. tert-Butylammonium fluoride (TBAF, 1.0 N solution in THF, 3.0 mL) was added dropwise, and the solution was stirred at –78 °C for 3 h; then another portion of TBAF (1.0 mL) was added, and stirring was continued for 1 h. The reaction mixture was quenched with a solution of acetic acid (0.2 g) in THF (15 mL) at –78 °C. The contents were poured into dichloromethane (100 mL) and washed with brine (150 mL) and water (150 mL). The organic layer was dried over MgSO4 and the solvent was removed by rotary evaporation. The product was purified by column chromatography (1.1 N petroleum ether, CH2Cl2). Yield: 1.07 g (98%). 1H NMR (CDCl3): δ 8.32 (d, 2H), 7.69 (d, 2H), 7.62 (m, 4H), 7.39 (d, 2H), 7.33 (d, 2H), 6.35–7.25 (m, 50 H), 4.41–5.26 (m, 12H), 1.01–2.41 (m, 116H). GPC (THF): PDI 1.05; M, 1860 (9, 9). GPC (THF): PDI 1.10; M, 1540 (5, 5).

4-[4-(Dimethylthexylsiloxy)-4-biphenyl]carboxylate Poly(styrene-b-isoprene) 4-Carboxylate (0.9 g, 0.4 mmol), DPTS (0.2 g, 0.8 mmol), and dichloromethane (20 mL) was stirred at room temperature for 5 min. Disopropylcarbodiimide (0.5 mL, 1.6 mmol, δ 0.806) was added dropwise, and the solution was stirred overnight at room temperature. The solution was diluted with dichloromethane (30 mL) and then washed with water (50 mL). The organic layer was dried over MgSO4, and then the solvent was removed by rotary evaporation. The product was isolated by column chromatography (CDCl3) as a white solid. Yield: 1.07 g (98%). 1H NMR (CDCl3): δ 8.32 (d, 2H), 7.67 (d, 2H), 7.62 (m, 4H), 7.39 (d, 2H), 7.38 (d, 2H), 7.30 (d, 2H), 6.57–7.25 (m, 50 H), 4.41–5.26 (m, 12H), 1.01–2.41 (m, 116H). GPC (THF): PDI 1.05; M, 1860 (9, 9). GPC (THF): PDI 1.10; M, 1540 (5, 5).

4-[4-(Dimethylthexylsiloxy)-4-biphenyl]carboxylate Poly(styrene-b-isoprene) 4-Carboxylate (0.9 g, 0.4 mmol), DPTS (0.2 g, 0.8 mmol), and dichloromethane (20 mL) was stirred at room temperature for 5 min. Disopropylcarbodiimide (0.5 mL, 1.6 mmol, δ 0.806) was added dropwise, and the solution was stirred overnight at room temperature. The solution was diluted with dichloromethane (30 mL) and then washed with water (50 mL). The organic layer was dried over MgSO4, and then the solvent was removed by rotary evaporation. The product was isolated by column chromatography (CDCl3) as a white solid. Yield: 1.07 g (98%). 1H NMR (CDCl3): δ 8.32 (d, 2H), 8.26 (d, 2H), 7.75 (d, 2H), 7.68 (m, 2H), 7.60 (d, 4H), 7.52 (d, 2H), 7.38 (d, 2H), 7.30 (d, 2H), 6.35–7.25 (m, 50 H), 4.41–5.26 (m, 12H), 1.01–2.41 (m, 116H). GPC (THF): PDI 1.05; M, 1860 (9, 9). GPC (THF): PDI 1.10; M, 1540 (5, 5).
biphenol (0.13 g, 0.7 mmol), DPTS (0.23 g, 0.8 mmol), and dichloromethane (10 mL) were placed in a flask. Diisopropylcarbodiimide (0.5 mL, 0.8 mmol, 0.806) was added, and the solution was stirred overnight at room temperature. The resulting precipitate was removed via filtration, and the solvent was removed by rotary evaporation. The product was isolated by column chromatography (CH₂Cl₂) as a white solid. Yield: 0.9 g (65%).¹¹H NMR (CDCl₃): δ 7.68 (d, 2H), 6.35–7.25 (m, 32 H), 4.41–5.26 (m, 7H), 1.01–2.41 (m, 70H).

4-[4-[4-[Dimethylthexyloxilaryl]-4-biphenylcarbonyloxy]-4-biphenylcarbonyloxy]-4-biphenylcarbonyloxy]biphenyl Poly(styrene-b-isoprene) 4-Carboxylate. A solution of 4-[4-[Dimethylthexyloxilaryl]-4-biphenylcarbonyloxy]-4-biphenylcarbonyloxy]biphenyl Poly(styrene-b-isoprene) 4-carboxylate (0.2 g, 0.6 mmol), DPTS (0.2 g, 0.8 mmol), and dichloromethane (20 mL) was stirred at room temperature for 5 min. Diisopropylcarbodiimide (0.5 mL, 1.6 mmol, δ 0.806) was added dropwise, and the solution was stirred overnight at room temperature. The solution was diluted with dichloromethane (30 mL), then washed with water (50 mL). The organic layer was dried over MgSO₄, then the solvent was removed by rotary evaporation. The product was isolated by column chromatography (CH₂Cl₂) as a white solid. Yield: 0.95 g (78%).¹¹H NMR (CDCl₃): δ 8.32 (d, 4H), 8.26 (d, 4H), 7.75 (d, 4H), 7.68 (m, 2H), 7.60 (d, 4H), 7.52 (d, 2H), 7.38 (d, 2H), 7.30 (d, 2H), 6.35–7.26 (m, 50 H), 4.41–5.26 (m, 12H), 1.01–2.41 (m, 116H), 0.92 (s, 12H), 0.30 (s, 6H). GPC (THF): PDI = 1.07; Mₐ = 5100.

4-[4-[4-Hydroxy-4-biphenylcarbonyloxy]-4-biphenylcarbonyloxy]biphenyl Poly(styrene-b-isoprene) 4-Carboxylate (5). A flask was charged with 4-[4-[4-[4-[Dimethylthexyloxilaryl]-4-biphenylcarbonyloxy]-4-biphenylcarbonyloxy]biphenyl poly(styrene-b-isoprene) 4-carboxylate (0.9 g, 0.4 mmol) and THF (20 mL). The solution was cooled to −78 °C in a dry ice/acetone slush bath, and then TBAF (1.0 N solution in THF, 3.0 mL) was added slowly and the reaction mixture was stirred for 3 h. A second portion of TBAF (1.0 mL) was then added, and the solution was stirred for 1 h at −78 °C. The reaction mixture was quenched with a solution of acetic acid (0.2 g) in THF (15 mL) at −78 °C. The contents were poured into dichloromethane (100 mL) and washed with water (100 mL). The organic layer was dried over MgSO₄, and then the solvent was removed by rotary evaporation. The product was isolated by column chromatography (1:10, MeOH/CH₂Cl₂) as a white solid. Yield: 0.81 g (97%).¹¹H NMR (CDCl₃): δ 8.33 (d, 4H), 8.29 (d, 4H), 7.77 (d, 4H), 7.69 (m, 2H), 7.62 (d, 4H), 7.55 (d, 2H), 7.37 (d, 2H), 7.31 (d, 2H), 6.35–7.25 (m, 48 H), 4.41–5.26 (m, 12H), 1.01–2.41 (m, 113H).

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References and Notes

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